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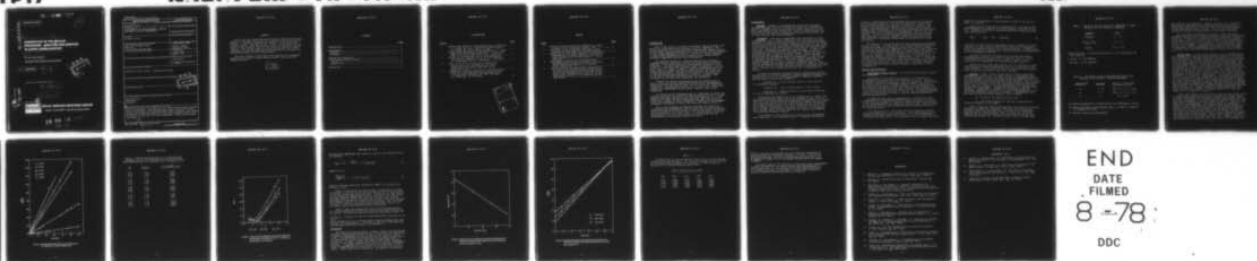
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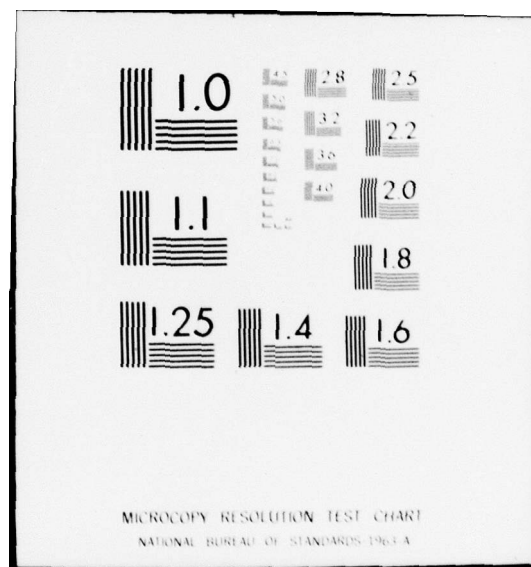
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**THIOSULFATE IN THE WOLLAK  
PROCEDURE - ANALYSIS AND KINETICS  
IN ACIDIC FORMALDEHYDE**

BY WILLIAM P. KILROY

RESEARCH AND TECHNOLOGY DEPARTMENT

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SUMMARY

One of the high energy density batteries currently being considered by the Navy for future use in mines is the Li-SO<sub>2</sub> reserve battery. A question regarding the safety of this battery has recently arisen. This may be due, in part, to the fact that the nature of the cathodic reaction that occurs on discharge remains unknown. This is the first in a series of reports in a recent undertaking to develop experimental procedures for analyzing the discharge products of the Li-SO<sub>2</sub> battery.

The work leading to this report was supported by Independent Research at the Naval Surface Weapons Center under Task Area Number ZR0130101.

*J. R. Dixon*  
J. R. DIXON  
By Direction

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## INTRODUCTION

This is the first in a series of technical reports dealing with analytical investigations of mixtures of sulfur compounds. The overall objective is to quantitatively determine the complex mixture of oxy-sulfur compounds that may form at the cathode current collector of the  $\text{Li}/\text{CH}_3\text{CN}-\text{LiAsF}_6/\text{SO}_2$  battery. A variety of sulfur compounds is conceivable depending on such variables as  $\text{SO}_2$  concentration, discharge temperature and the rate of discharge.

The classical method for analyzing mixtures of oxy-sulfur compounds such as dithionite, sulfite and thiosulfate was devised by Wollak.<sup>1</sup> The method consists of performing a series of three iodometric titrations under different reaction conditions. In the first titer, the sample is added to aqueous formaldehyde which complexes sulfite, cleaves dithionite quantitatively and leaves the thiosulfate unreacted. The sum of the dithionite and thiosulfate is then determined simultaneously by iodimetry. A second titer of the Wollak procedure determines only the thiosulfate. The difference in the two titers represents the dithionite.

Latimer<sup>2</sup> has studied the procedure for the second titer in detail and has found the thiosulfate determination unacceptable, whereas Zubritsky and Danehy<sup>3</sup> have found the value for thiosulfate acceptable. Of particular interest is the first titer, where thiosulfate and formaldehyde may be present together under acidic conditions.

At low pH, the acid decomposition of thiosulfate to sulfur and bisulfite has been the subject of numerous papers,<sup>4-12</sup> and a formaldehyde-thiosulfate reaction product has been reported.<sup>13</sup> In acid solutions of higher pH where thiosulfate has been reported to be stable with respect to sulfur formation,<sup>14</sup> addition of formaldehyde decomposes thiosulfate to sulfur and bisulfite quantitatively.<sup>15</sup>

Due to the diversity of reports concerning the behavior of thiosulfate and formaldehyde in acidic solution, it was decided to study the kinetics of this system in order to determine the validity of the procedure of the first titer. If reaction occurs, then the thiosulfate in the two titers would not be equivalent and the determination of dithionite would be in error.

EXPERIMENTAL

REAGENTS. Reagent 37% formaldehyde neutralized with NaOH solution was used. Fresh thiosulfate solutions were standardized against a standard  $\text{KIO}_3$  solution and the iodine solutions in turn were standardized by the thiosulfate. Since the Wollak method uses acetic acid, high capacity sodium acetate-acetic acid buffers, 2M in total acetate, were used throughout.

PROCEDURE. Four sets of experiments were performed in order to determine: (a) if acidic conditions could arise when oxy-sulfur compounds are added to  $\text{CH}_2\text{O}-\text{H}_2\text{O}$  mixtures, (b) the accuracy of determination of thiosulfate in various  $\text{CH}_2\text{O}-\text{H}_2\text{O}$  solutions, (c) the nature of the products of any thiosulfate-formaldehyde reaction under acidic conditions, and (d) how the kinetics of the reaction (effect of pH, time, etc.) influenced the analysis of thiosulfate. In the first titration in the Wollak method, the sample is added to aqueous formaldehyde that is neutral to Methyl Orange. Since the resulting solution can have a range of pH values, and a reaction between thiosulfate and formaldehyde might be pH dependent, it was decided to determine the pH range of various oxy-sulphur compounds in the recommended  $\text{CH}_2\text{O}-\text{H}_2\text{O}$  mixture. This was accomplished by adding separate samples of 0.1 and 0.5 grams of anhydrous sulfite, thiosulfate pentahydrate and Baker purified dithionite (90%) to a mixture consisting of 10 ml 37%  $\text{CH}_2\text{O}$  (adjusted to pH-5.0 with NaOH) and 5 ml water. The pH of the resulting solutions were recorded after 5 minutes.

In order to ascertain how quantitatively thiosulfate could be determined by this Wollak procedure, weighed samples of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  ranging from 0.4 to 2.0 m moles were added to  $\text{CH}_2\text{O}-\text{H}_2\text{O}$  solutions. The following solutions were prepared:

Solution (A) - 35 ml 37%  $\text{CH}_2\text{O}$  (pH  $\approx$  5), 50 ml  $\text{H}_2\text{O}$  and 0.10 anhydrous  $\text{Na}_2\text{CO}_3$ .<sup>16</sup>

Solution (B) - 10 ml 37%  $\text{CH}_2\text{O}$  (pH  $\approx$  5) and 5 ml  $\text{H}_2\text{O}$ .

Solution (C) - same as Solution (B) but also containing 1 to 2 ml of HAC-NaAc 4.76 buffer.

Thiosulfate was added to 15 ml of solution (A) in a small vial, stirred two minutes, transferred to an erlenmeyer flask, 50 ml of water and 2 ml of 20% acetic acid added and titrated with 0.1N iodine. With solutions (B) and (C) the thiosulfate was added, and the solutions were allowed to stand in a small closed vial for 20 minutes. The contents of solutions B and C were transferred to 500 ml volumetric flasks, and diluted to the mark with water, 50 ml aliquots were removed, 200 ml of water added and the analysis performed by the prescribed iodimetric method.

The products of the reaction of thiosulfate and formaldehyde were identified in the following manner: A standard thiosulfate



solution, containing excess formaldehyde and buffered with acetate at pH 4.76 was allowed to react to near completion. Qualitative tests showed the absence of sulfide, dithionite or sulfate. The residue, confirmed by X-ray analysis to be sulfur, was filtered, washed, dried and weighed. The unreacted thiosulfate was determined iodimetrically from an aliquot of the solution. Sulfite does not interfere due to the formation of formaldehyde bisulfite in acidic solution. Sulfite and the unreacted thiosulfate were determined simultaneously by oxidizing another aliquot of the solution with basic peroxide, acidifying, adding  $\text{BaCl}_2$  and weighing the sulfate precipitate.

The kinetics of the above reaction was studied by the following general procedure. A known aliquot of freshly prepared thiosulfate solution was added to a volumetric flask, buffer solution added, followed by any additional components such as water or salt solutions and the time recorded upon addition of a known aliquot of neutral  $\text{CH}_2\text{O}$ . The volumetric flask was adjusted to the mark with buffer and the solution stored in the dark at  $26^\circ\text{C} \pm 1^\circ\text{C}$ . At intervals, an aliquot was removed, diluted with approximately 150 ml of water and titrated with standard iodine to a faint yellow color. At high  $\text{CH}_2\text{O}$  concentrations, the iodine color fades and the end point was taken as a 20-second duration of the yellow color. The pH was monitored throughout and was found to remain unchanged, regardless of  $\text{CH}_2\text{O}$  concentration.

## RESULTS AND DISCUSSION

PRELIMINARY KINETIC STUDIES. The following preliminary studies were conducted:

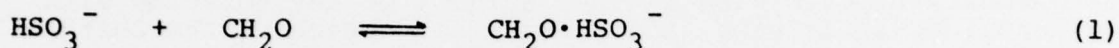
The stability of thiosulfate solutions in the absence of formaldehyde was studied over a pH range of 4.3 to 6.0. Aliquots of standard thiosulfate solutions in various pH buffers, were removed at several intervals, formaldehyde added to complex any sulfite, and titrated with iodine. A small decrease in the thiosulfate concentration was observed over the first few hours which returned to the original concentration after about 8 hours. The maximum decrease (1.5%) occurred at pH 4.76 after 2.5 hours. This unexplained phenomenon may be associated with some of the observations reported by Bassett and Durrant.<sup>14</sup>

By comparing the rates of disappearance of thiosulfate from formaldehyde and formaldehyde-methyl alcohol solutions, it was confirmed that the presence of the methyl alcohol preservative present in the formaldehyde did not affect the reaction rate. Methyl alcohol was found not to react with standard iodine on standing five hours in a 4.76 pH buffer.

The reactivity of a 1.34 M  $\text{CH}_2\text{O}$  solution containing standard iodine was observed in a 4.76 pH buffer. The iodine determined by standard thiosulfate reacted at the rate of  $4 \times 10^{-4}$  equivalents/liter/hour over four hours. This indicates that the fading end point

observed in the presence of large amounts of  $\text{CH}_2\text{O}$  is not due to a  $\text{CH}_2\text{O} - \text{I}_2$  reaction.

Solutions of various sulfite concentrations in different  $\text{CH}_2\text{O}$  concentrations were prepared in buffers ranging in pH from 1.2 to 9.7. Immediate titration of these solutions with iodine confirmed that the equilibria



is shifted in favor of the formaldehyde bisulfite complex in acidic solution. In acid solution, one drop of iodine gave a permanent yellow color showing that no free bisulfite existed. In basic solution, the iodine is consumed since increasing pH favors decomposition of the formaldehyde bisulfite.

The rate of reaction of iodine with the expected product, formaldehyde bisulfite, was studied at pH 4.76. Due to a shift in the equilibria of Equation (1), a reaction occurs but at a negligible rate compared to the thiosulfate-iodine reaction.

A positive salt effect was observed for the reaction of 0.01M thiosulfate and 1.34M formaldehyde at pH 4.76 in solutions of low ionic strength. To avoid salt effects, kinetic data were obtained under conditions of constant high ionic strength.

ANALYSIS. Table 1 shows the pH range of various oxy-sulfur compounds in a mixture of 5 ml water and 10 ml formaldehyde where the formaldehyde is neutral to methyl orange as suggested by Wollak. Actually the pH of the  $\text{CH}_2\text{O}-\text{H}_2\text{O}$  mixtures was approximately 5.0. In this unbuffered solution, sulfite solutions are basic. The dithionite solution is distinctly acidic and the resulting pH would have been still lower if it were not for the approximately 10% sulfite-thiosulfate impurity present. (Commercial dithionite is typically only 90% pure.) Unexpectedly, the pH of the thiosulfate solution increases, perhaps due to formation of some formaldehyde bisulfite which then generates sulfite at a pH above 7. Consequently, the pH range of these solutions depends on the following:

- (a) the pH of the  $\text{CH}_2\text{O}-\text{H}_2\text{O}$  mixture and
- (b) the relative amounts of sulfite, thiosulfate and dithionite present in the sample.

Table 2 shows the results obtained when variations of the Wollak procedure are applied to standards containing only thiosulfate. Accurate results are obtained only if the pH of the thiosulfate- $\text{CH}_2\text{O}-\text{H}_2\text{O}$  mixture remains greater than 7.0 before the titration. Solution (A) is basic both before and after addition of the thiosulfate and Solution (B), initially acidic at pH 5, becomes basic

Table 1. The pH of Various Oxy-sulfur Compounds in a pH~5 Solution of a 2:1 Mixture of  $\text{CH}_2\text{O} \cdot \text{H}_2\text{O}$ 

<u>Compound</u>	<u>pH ‡</u>
$\text{Na}_2\text{S}_2\text{O}_4$ *	5.7 - 6.3
$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	7.5 - 7.9
$\text{Na}_2\text{SO}_3$	10.5 - 11.3

\* Baker Purified - contains 90% dithionite, 2.5% thiosulfate and 7.5% bisulfite

‡ Low pH - 0.1 gm compound

High pH - 0.5 gm compound

Table 2. The Effect of pH of  $\text{CH}_2\text{O} \cdot \text{H}_2\text{O}$  Solutions in the Recovery of Thiosulfate in the Wollak Method

<u>Solutions</u> (a)	<u>pH range</u>	<u>%<math>\text{Na}_2\text{S}_2\text{O}_3</math> recovered</u> (b)
A	7 - 10	100.1 (n = 4, s = 0.4)
B	7 - 9	100.2 (n = 5, s = 0.4)
C	< 7	90 - 95 (c)

(a) Solution preparation is described in the experimental section.

(b) Sample size was 2 m mole  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ; n = number of samples; s = standard deviation.

(c) The low results are pH dependent.



upon addition of thiosulfate. However, Solution (C), buffered to remain acidic upon addition of thiosulfate, gave low values for thiosulfate, generally 5 to 10% low when the thiosulfate- $\text{CH}_2\text{O}$ - $\text{H}_2\text{O}$  mixture remained 20 minutes at pH~5. Dilution of these acidic solutions to 500 ml with water gave rise to a white turbidity.

The thiosulfate-formaldehyde reaction in a pH 4.76 buffer proceeds quantitatively to form the products sulfur and formaldehyde-bisulfite. Analysis of a standard solution containing 5 m moles thiosulfate in which 4.9 m moles was allowed to react produced 4.9 m moles sulfur and 4.9 m moles bisulfite. The nature and the extent of the reaction appears to be dependent on the pH and  $\text{CH}_2\text{O}$  concentration. For example, a compound with the empirical formula  $\text{CH}_2\text{S}$  (corresponding to thioformaldehyde) forms when 12 M HCl is added to concentrated thiosulfate-formaldehyde solutions to give a pH of 1.0.

**KINETIC DATA.** In this study, reaction rate is defined as the rate of loss of thiosulfate as determined by iodimetric titration. The experimentally observed pseudo rate constants,  $k$ , were obtained under conditions of constant hydrogen ion concentration maintained by large buffer capacity and in the presence of excess  $\text{CH}_2\text{O}$ . The rate of disappearance of thiosulfate was found to be second order in thiosulfate. Figure 1 illustrates the second order reaction of thiosulfate at different molar concentrations in a buffered solution of constant pH 4.3 and ionic strength 0.5. The slopes (rate constants) of the second order curves, in which the reciprocal molar thiosulfate concentration is plotted against time, were found to be independent of thiosulfate concentration. This necessary condition, that the rate constant was independent of thiosulfate concentration in the presence of a large excess of  $\text{CH}_2\text{O}$ , was similarly verified for other constant pH values. The results are tabulated in Table 3. Note that with increasing thiosulfate concentration, the y intercept has an increasing tendency to diverge from the original thiosulfate concentration. For the 0.01M, 0.03M and 0.06M thiosulfate solutions, the y intercepts are .0094M, .028M and 0.056M respectively. The effect of pH on the reaction of 0.01M thiosulfate in 1.34M  $\text{CH}_2\text{O}$  (Table 3) is illustrated in Figure 2.

Since salt effects were observed to influence the kinetic data, it was decided to observe the kinetic behavior at constant ionic strength. The pseudo rate constants for the second order reaction of 0.03M thiosulfate in various excess  $\text{CH}_2\text{O}$  concentrations at a constant ionic strength of 1.07 are listed in Table 4. Since the rate expression is pH dependent, the slope of  $\log k$  vs. pH curves, Figure 3, under conditions of a constant excess  $\text{CH}_2\text{O}$  concentration should give the order of hydrogen ion. From the data of Table 4, plotting  $\log k$  vs. pH curves reveal that increasing the  $\text{CH}_2\text{O}$  concentration increases the nonlinearity of the curves. A break in the curve occurs between pH 4.30 and 4.76 which indicates a complex rate expression involving  $\text{CH}_2\text{O}$ . Using a least squares treatment on that portion of the curves above pH 4.76, it appears that as the  $\text{CH}_2\text{O}$  concentration approaches zero, the order of the hydrogen ion

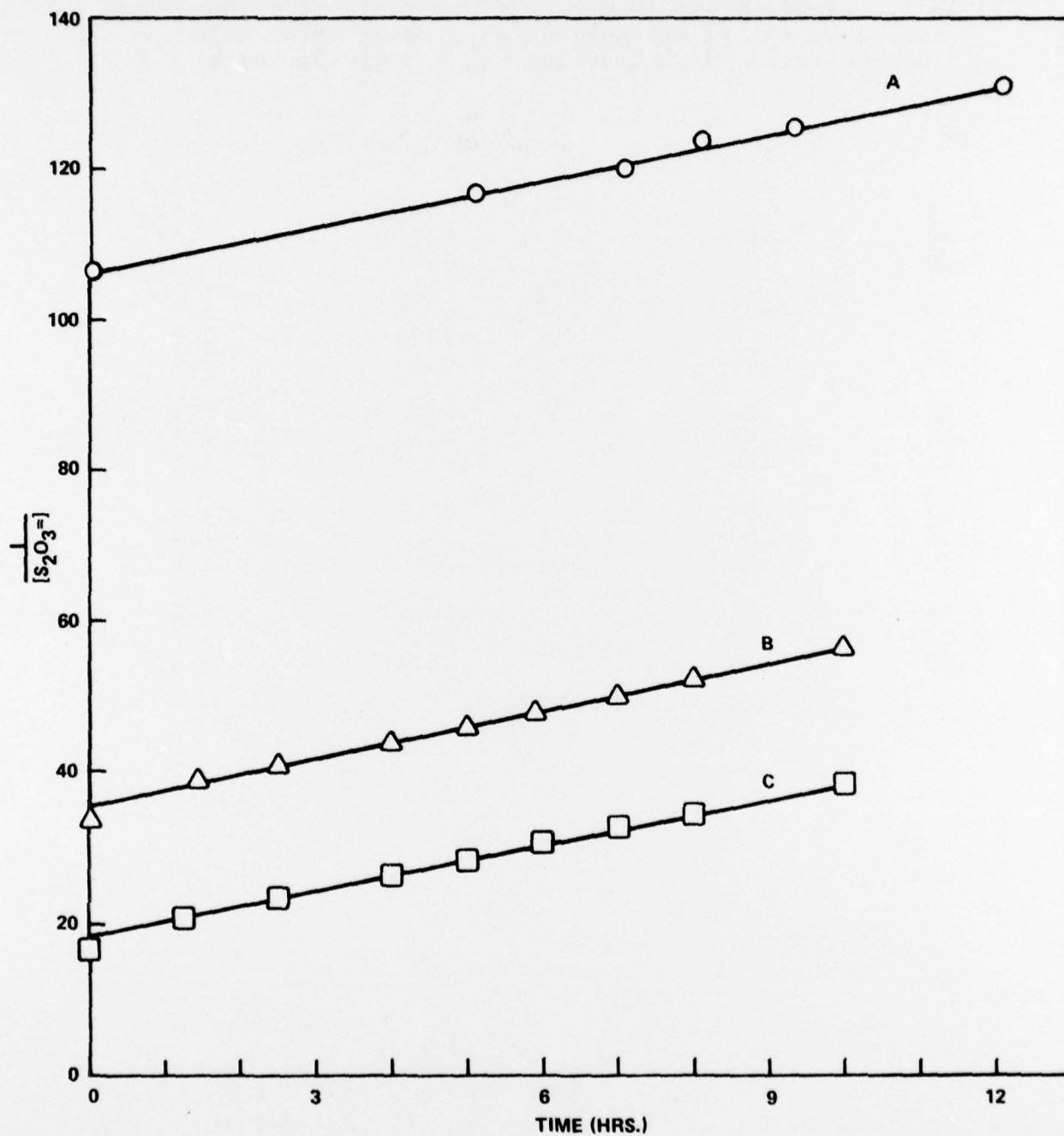


FIGURE 1. SECOND ORDER REACTION OF THIOSULFATE WITH 1.34 M  $CH_2O$  AT CONSTANT pH 4.3. THIOSULFATE CONCENTRATION: (A) 0.01 M; (B) 0.03 M; (C) 0.06 M

Table 3. Pseudo Second Order Rate Constants of Thiosulfate Decomposition in Excess  $\text{CH}_2\text{O}$  as a Function of Molar Concentration of Thiosulfate ( $\mu$  = Ionic Strength)

pH	$\text{M}(\text{S}_2\text{O}_3^{=})$	$\frac{k}{(\text{liters/mole} \cdot \text{min})}$	$\mu$
4.30	.01	.0341	.51
4.30	.03	.0346	.57
4.30	.06	.0343	.59
4.76	.01	.0284	1.1
4.76	.03	.0286	1.1
4.76	.06	.0280	1.1
4.88	.01	.0240	1.1
4.88	.03	.0230	1.1
4.88	.06	.0234	1.1
5.33	.01	.00990	1.4
5.33	.03	.0101	1.4
5.33	.06	.00980	1.4
6.05	.01	.00228	1.6
6.05	.03	.00200	1.6
6.05	.06	.00201	1.6



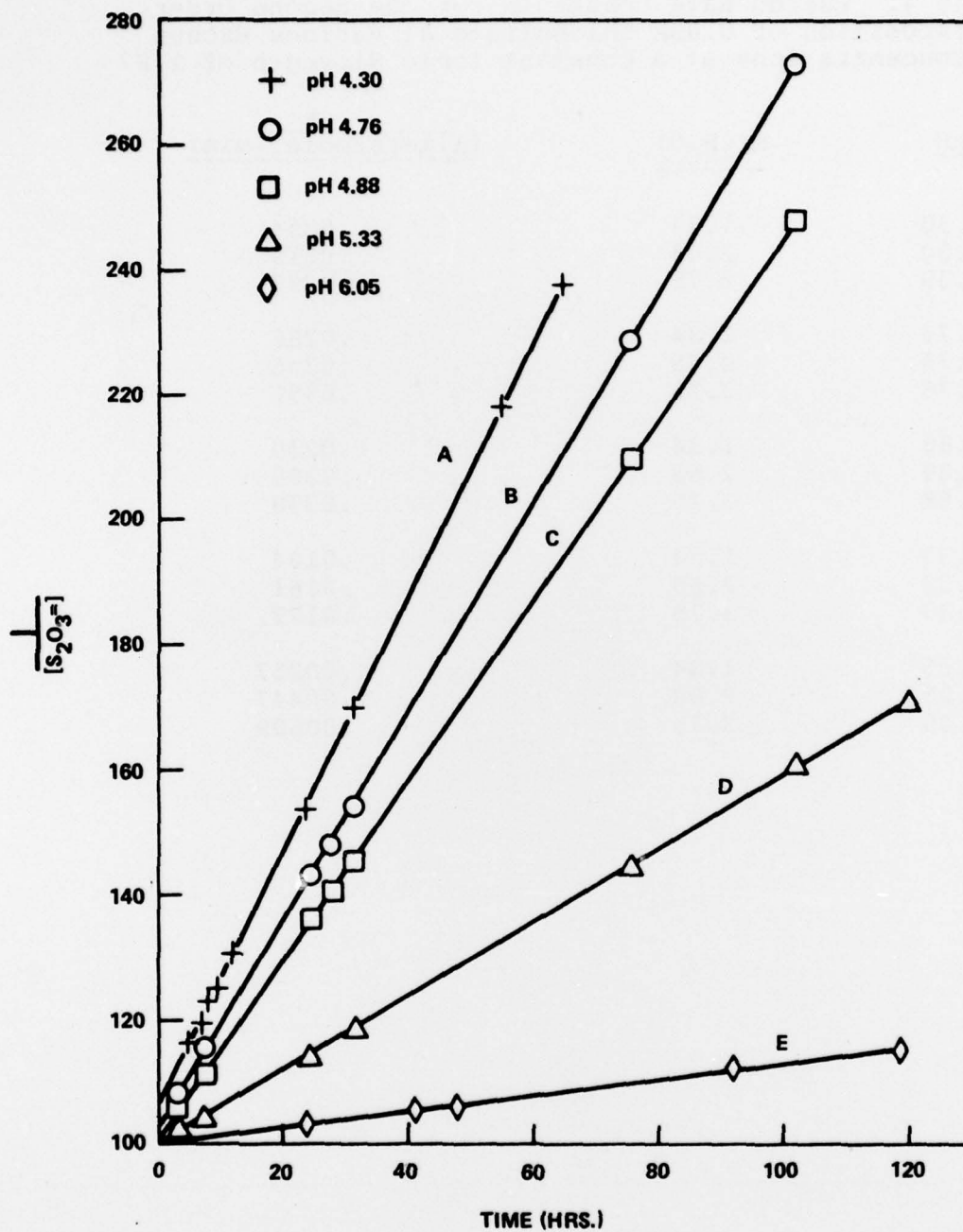


FIGURE 2. SECOND ORDER REACTION OF 0.01 M THIOSULFATE  
IN 1.34 M CH<sub>2</sub>O AT VARIOUS CONSTANT pH

Table 4. Pseudo Rate Constants for the Second Order Decomposition of 0.03M Thiosulfate at Various Excess  $\text{CH}_2\text{O}$  Concentrations at a Constant Ionic Strength of 1.07

<u>pH</u>	<u>M(<math>\text{CH}_2\text{O}</math>)</u>	<u><math>\frac{k}{\text{(liters/mole.-min)}}</math></u>
4.30	1.34	.0354
4.30	2.68	.0319
4.30	3.75	.0293
4.76	1.34	.0286
4.76	2.68	.0346
4.76	3.75	.0356
4.88	1.34	.0230
4.88	2.68	.0309
4.88	3.75	.0330
5.33	1.34	.0104
5.33	2.68	.0161
5.33	3.75	.0179
6.05	1.34	.00257
6.05	2.68	.00447
6.05	3.75	.00609

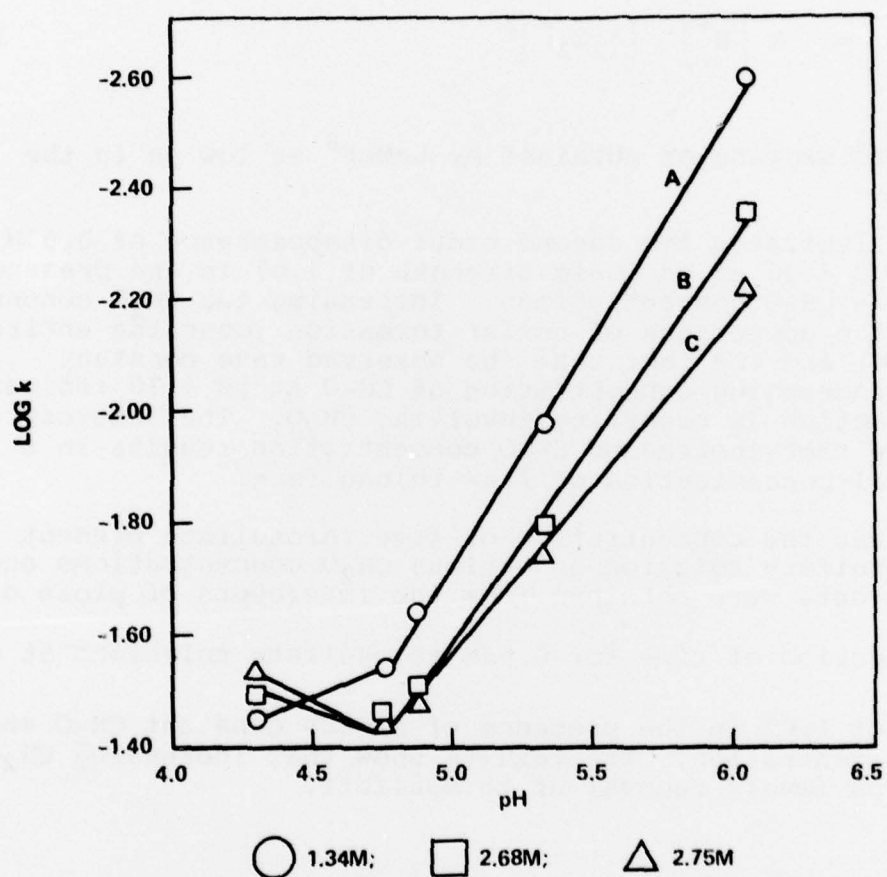
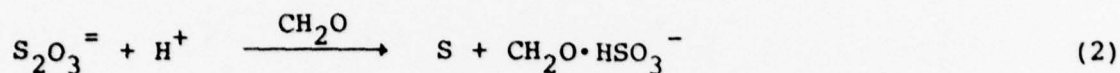


FIGURE 3. LOG OF THE RATE CONSTANT FOR A 0.03 M THIOSULFATE SOLUTION AS A FUNCTION OF pH FOR: (A) 1.34 M  $\text{CH}_2\text{O}$ ; (B) 2.68 M  $\text{CH}_2\text{O}$ ; (C) 3.75 M  $\text{CH}_2\text{O}$

concentration approaches one, Figure 4, and the rate expression for the reaction



appears to be

$$\frac{-d[\text{S}_2\text{O}_3^{=}]}{dt} = k [\text{H}^+]^1 [\text{S}_2\text{O}_3^{=}]^2 \quad (3)$$

which is the rate expression obtained by LaMer<sup>6</sup> at low pH in the absence of  $\text{CH}_2\text{O}$ .

Figure 5 illustrates the second order disappearance of 0.03M thiosulfate at pH 4.30 at an ionic strength of 1.07 in the presence of various excess  $\text{CH}_2\text{O}$  concentrations. Increasing the  $\text{CH}_2\text{O}$  concentration delays the appearance of sulfur formation (over the entire pH range studied) and the fact that the observed rate constant decreases with increasing concentration of  $\text{CH}_2\text{O}$  at pH 4.30 indicates that another reaction is occurring involving  $\text{CH}_2\text{O}$ . The intercepts in Figure 5 show that increasing  $\text{CH}_2\text{O}$  concentration results in a decreased initial concentration of free thiosulfate.

Table 5 gives the concentration of free thiosulfate present in a 0.03M thiosulfate solution at various  $\text{CH}_2\text{O}$  concentrations and pH values. The data were obtained from the intercepts of plots of  $\frac{1}{[\text{S}_2\text{O}_3^{=}]}$  as a function of time for 0.03M thiosulfate solutions at an ionic strength of 1.07 in the presence of excess constant  $\text{CH}_2\text{O}$  and hydrogen ion concentration. The results show that increasing  $\text{CH}_2\text{O}$  and decreasing pH favors removal of thiosulfate.

#### CONCLUSION

The analytical data presented in Table 2 shows that the Wollak procedure used for determining the sum of dithionite and thiosulfate in aqueous formaldehyde can be in error if the solution remains acidic. The procedure of neutralizing  $\text{CH}_2\text{O}$  to methyl orange (pH~5) is insufficient for mixtures containing a large proportion of dithionite. As Table 1 shows, the ratio of oxy-sulfur compounds present in the sample determines the pH of the aqueous formaldehyde solution. A  $\text{CH}_2\text{O}$ - $\text{H}_2\text{O}$  mixture (initial pH~5) containing a weight ratio of approximately 4:1 dithionite to thiosulfate can still be acidic. Under these acidic conditions, the amount of thiosulfate



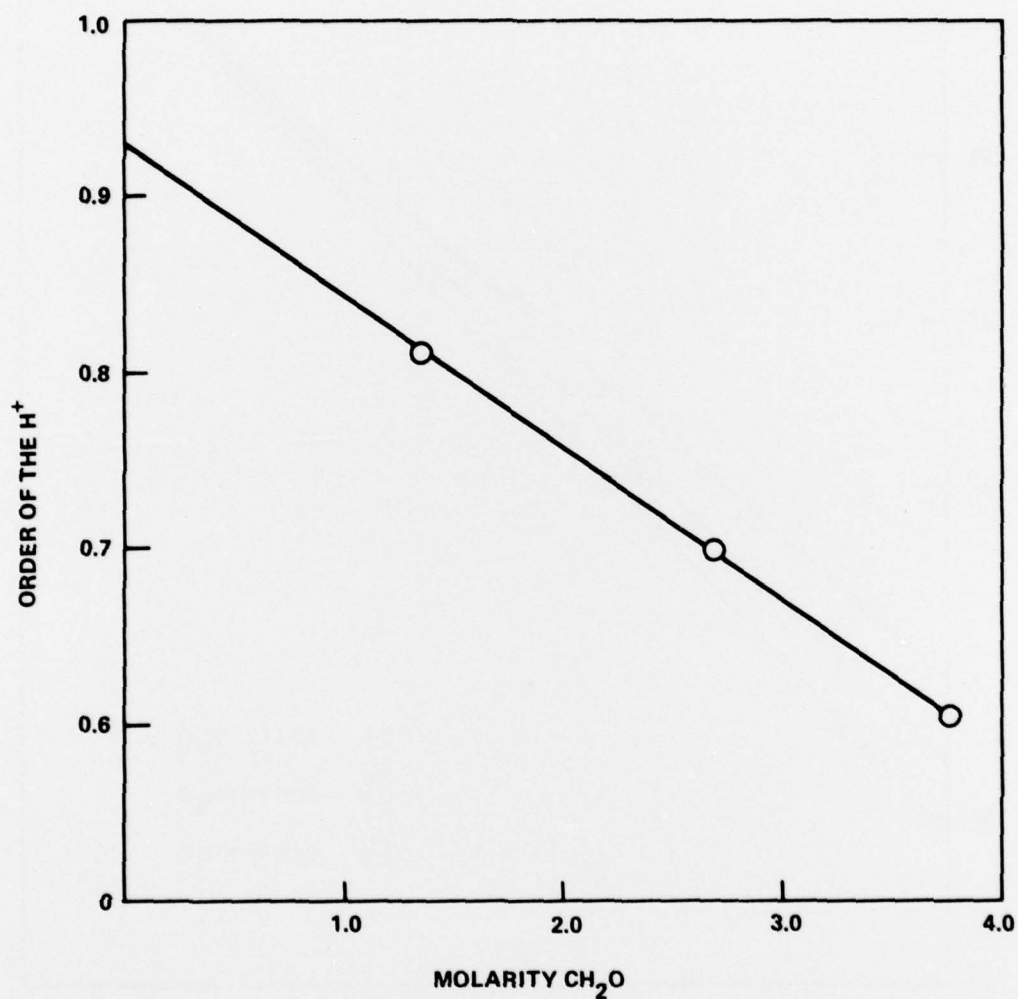


FIGURE 4. ORDER OF  $H^+$  AS A FUNCTION OF EXCESS  $CH_2O$  CONCENTRATION FOR THE REACTION OF 0.03 M THIOSULFATE WITH EXCESS  $CH_2O$  OVER THE pH RANGE 4.7 TO 6.0

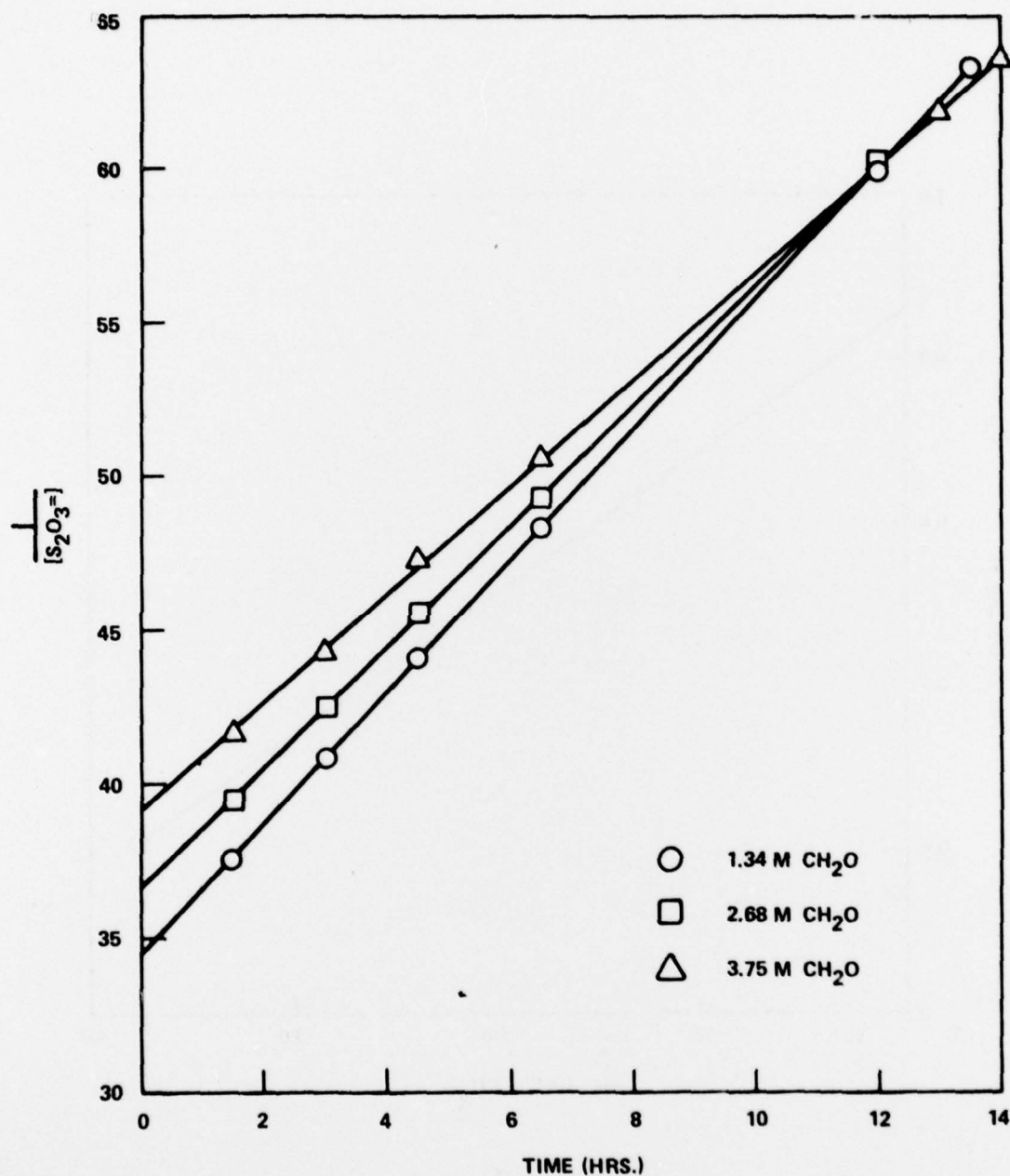


FIGURE 5. SECOND ORDER REACTION CURVES FOR 0.03 M THIOSULFATE REACTION IN VARIOUS  $CH_2O$  CONCENTRATIONS AT pH 4.30 AND IONIC STRENGTH 1.07



Table 5

Concentration of free thiosulfate (moles/liter) at various  $\text{CH}_2\text{O}$  concentrations and pH values. The data was obtained as the intercept of the second order decomposition curves of a 0.03M thiosulfate solution at the tabulated pH and  $\text{CH}_2\text{O}$  values.

	<u>Molar Concentration of <math>\text{CH}_2\text{O}</math></u>			
<u>pH</u>	<u>5.36</u>	<u>3.75</u>	<u>2.68</u>	<u>1.34</u>
4.30	.0234	.0255	.0272	.0291
4.76	.0266	.0274	.0280	.0298
4.88	.0269	.0280	.0286	.0299
5.33	.0287	.0290	.0292	.0299
6.05	.0297	.0298	.0299	.0300

found is low and not equivalent to the thiosulfate determined in the second part of the Wollak procedure. In order to avoid such analytical problems, the pH of the  $\text{CH}_2\text{O}-\text{H}_2\text{O}$  mixture should first be adjusted to about 8 to 9 with  $\text{NaOH}$  or  $\text{Na}_2\text{CO}_3$  before the sample is added.

A kinetic study of the reaction of thiosulfate with formaldehyde in acid, confirms that the pseudo second order disappearance of thiosulfate (Table 5) is a function of pH and  $\text{CH}_2\text{O}$  concentration. It is beyond the scope of this paper to discuss the unresolved question regarding the mechanism of this reaction.

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